

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification <sup>6</sup> :

C11D 3/39

A1

(11) International Publication Number:

WO 95/13352

(43) International Publication Date:

18 May 1995 (18.05.95)

(21) International Application Number: PCT/EP94/03656

(22) International Filing Date: 3 November 1994 (03.11.94)

(30) Priority Data:

08/151717

12 November 1993 (12.11.93) US

08/278664

21 July 1994 (21.07.94) US

(71) Applicant (for all designated States except AU BB CA GB IE LK MN MW NZ SD): UNILEVER N.V. [NL/NL]; Weena 455, NL-3013 AL Rotterdam (NL).

(71) Applicant (for AU BB CA GB IE LK MN MW NZ SD only): UNILEVER PLC [GB/GB]; unilever House, Blackfriars, London EC4 4BQ (GB).

(72) Inventors: MADISON, Stephen, Alan; 24 Oriole Road, New City, NY 10956 (US). COOPE, Janet, Lynn; 20 Lawton Avenue, Cliffside Park, NJ 07010 (US).

(81) Designated States: AM, AT, AU, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, ES, FI, GB, GE, HU, JP, KE, KG, KP, KR, KZ, LK, LT, LV, MD, MG, MN, MW, NL, NO, NZ, PL, PT, RO, RU, SD, SE, SI, SK, TJ, TT, UA, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG), ARIPO patent (KE, MW, SD, SZ).

**Published**

*With international search report.*

*Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.*

(54) Title: IMINE QUATERNARY SALTS AS BLEACH CATALYSTS

**(57) Abstract**

Novel bleach catalysts, a method for bleaching substrates using these catalysts and detergent compositions containing the catalysts are reported. The bleaches are quaternary imine salts. Substrates such as fabrics may be bleached in an aqueous solution containing these salts and a peroxygen compound.

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LU	Luxembourg	TD	Chad
CS	Czechoslovakia	LV	Latvia	TG	Togo
CZ	Czech Republic	MC	Monaco	TJ	Tajikistan
DE	Germany	MD	Republic of Moldova	TT	Trinidad and Tobago
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America
FI	Finland	MN	Mongolia	UZ	Uzbekistan
FR	France			VN	Viet Nam
GA	Gabon				

IMINE QUATERNARY SALTS AS BLEACH CATALYSTS  
BACKGROUND OF THE INVENTION

Field of the Invention

- 5 The invention relates to a new type of low-temperature bleaching system and a method of cleaning substrates therewith.

The Related Art

- 10 Many household and personal care products are formulated with an active oxygen-releasing material to effect removal of stain and soil. Oxygen-releasing materials have an important limitation; their activity is extremely temperature-dependent. Temperatures in excess of 60°C are  
15 normally required to achieve any bleach effectiveness in an aqueous wash system. Especially for cleaning fabrics, high temperature operation is both economically and practically disadvantageous.
- 20 The art has partially solved the aforementioned problem through the use of activators. These activators, also known as bleach precursors, often appear in the form of carboxylic acid esters. In an aqueous liquor, anions of hydrogen peroxide react with the ester to generate the  
25 corresponding peroxyacid which oxidizes the stained substrate. Commercial application of this technology is found in certain fabric bleaching detergent powders incorporating tetraacetylenediamine (TAED) and sodium nonanoyloxybenzene sulfonate (SNOBS).
- 30 TAED is effective only under warm-hot wash conditions, i.e. above 30°C. Although this material is widely employed in Europe with laundry detergent, cold water consumer washing habits have not permitted use in the United States. SNOBS  
35 can operate at lower temperatures than TAED. For this reason, it has been commercialized in the United States but its performance could still be improved.

Another problem with carboxylic acid ester precursors such as TAED and SNOBS is that conversion to peracid is inefficient. A further difficulty is that they are not catalytic. Once the ester has been perhydrolyzed, it can no longer be recycled. Accordingly, relatively large amounts of precursor are necessary. Amounts as high as 8% may be necessary in a detergent formulation for bleaching fabrics. At such high use levels, cost for these relatively expensive chemicals is of major concern.

10

Recently there has been reported in U.S. Patent 5,047,163, U.S. Patent 5,045,233 and U.S. Patent 5,041,232, all to Batal and Madison, a system for activating bleach precursors based upon sulfonimines and N-sulfonyloxaziridines. While these compounds have been shown to be highly effective, even better catalysts are sought, especially for wash temperatures around 10°C, such as are experienced in Japan.

15

Outside the context of consumer products, there have been reports of catalytic oxidizing agents. Hanquet and co-workers, in a series of articles, reported preparation of a new class of stable olefin epoxidizing agents, namely oxaziridinium salts. See Hanquet, Lusinchi and Milliet, *Tet. Let.* (1988) 3941; Hanquet, Lusinchi and Milliet, *C.R. Acad. Sci. Paris* (1991) Series II, 625; and Hanquet, Lusinchi and Milliet, *Tet. Let.* (1988) 2817. These oxaziridinium salts were prepared by peracid or monopersulfate oxidation of a corresponding quaternary imine salt under alkaline conditions. Epoxides were reported to be formed from the reaction of olefins with the oxaziridinium salts. Reactions were conducted either in organic solvents or in organic solvent-water biphasic media. Beyond use as a synthetic tool, there is no suggestion of any possible application for quaternary imine salt chemistry to the problem of removing stains in consumer applications, such as in cleaning fabrics.

20

25

30

35

It is an object of the present invention to provide an improved bleaching system and detergent composition containing such system that operates over a wide temperature range including that of under 30°C.

It is another object of the present invention to provide novel bleach catalysts which are effective at relatively low concentrations, thereby achieving a cost-effective stain removal system.

A still further object of the present invention is to provide a method for bleaching stained substrates such as clothes, household hard surfaces including sinks, toilets and the like, and even dentures.

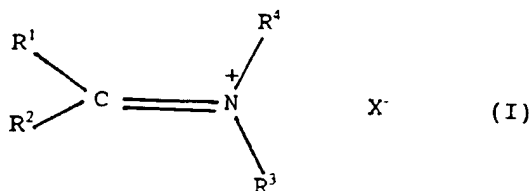
Other objects of the present invention will become more readily apparent through the following summary, detailed description and examples.

#### SUMMARY OF THE INVENTION

A bleaching composition is provided comprising:

(i) from about 1 to about 60% by weight of a peroxygen compound;

(ii) from about 0.01 to about 10% of an oxygen transfer agent whose structure is:



wherein:

R<sup>1</sup> and R<sup>4</sup> may be a substituted or unsubstituted radical selected from the group consisting of hydrogen, phenyl, aryl, heterocyclic ring, alkyl and cycloalkyl radicals;

$R^2$  may be a substituted or unsubstituted radical selected from the group consisting of hydrogen, phenyl, aryl, heterocyclic ring, alkyl, cycloalkyl, nitro, halo, cyano, alkoxy, keto, carboxylic and carboalkoxy radicals;

5  $R^3$  may be a substituted or unsubstituted radical selected from the group consisting of phenyl, aryl, heterocyclic ring, alkyl, cycloalkyl, nitro, halo, and cyano radicals;

$R^1$  with  $R^2$  and  $R^2$  with  $R^3$  may respectively together form  
10 a radical selected from the group consisting of cycloalkyl, polycyclo, heterocyclic and aromatic ring systems;

$X^-$  is a counterion stable in the presence of oxidizing agents; and

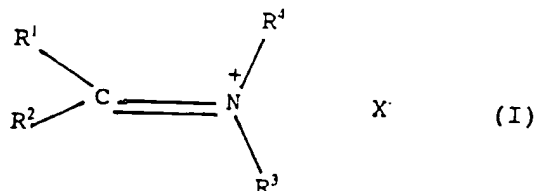
15 (iii) from about 0.5 to 50% of a surfactant.

Additionally, there is provided a method for bleaching a stained substrate comprising the step of applying to the stained substrate an aqueous solution comprising a peroxygen compound and an oxygen transfer agent whose  
20 structure is  $R^1R^2C=N^+R^3R^4X^-$  with radical groups as defined above, the mole ratio of peroxygen compound to oxygen transfer agent being from about 250:1 to about 1:2.

#### DETAILED DESCRIPTION

25 It has been found that certain types of quaternary imine salts can operate as catalysts on peroxygen compounds to transfer active oxygen to stains. Consumer and industrial articles can effectively be bleached to remove stains  
30 present on such articles. Thus, quaternary imine salt chemistry is more than a synthetic curiosity as in the conversion of olefins to epoxides reported by Hanquet et al. Unlike the Hanquet et al. reaction medium that requires an organic solvent, quaternary imine salts can be devised  
35 for use in completely aqueous wash systems.

Quaternary imine salts covered by the present invention are those whose structure is:



wherein:

$\text{R}^1$  and  $\text{R}^4$  may be hydrogen or a  $\text{C}_1$ - $\text{C}_{30}$  substituted or unsubstituted radical selected from the group consisting of phenyl, aryl, heterocyclic ring, alkyl and cycloalkyl radicals;

$\text{R}^2$  may be hydrogen or a  $\text{C}_1$ - $\text{C}_{30}$  substituted or unsubstituted radical selected from the group consisting of phenyl, aryl, heterocyclic ring, alkyl, cycloalkyl, nitro, halo, cyano, alkoxy, keto, carboxylic and carboalkoxy radicals;

$\text{R}^3$  may be a  $\text{C}_1$ - $\text{C}_{30}$  substituted or unsubstituted radical selected from the group consisting of phenyl, aryl, heterocyclic ring, alkyl, cycloalkyl, nitro, halo, and cyano radicals;

$\text{R}^1$  with  $\text{R}^2$  and  $\text{R}^2$  with  $\text{R}^3$  may respectively together form a cycloalkyl, polycyclo, heterocyclic or aromatic ring system;

$\text{X}^-$  is a counterion stable in the presence of oxidizing agents.

Heterocyclic rings according to this invention include cycloaliphatic and cycloaromatic-type radicals, incorporating an oxygen, sulfur and/or nitrogen atom within the ring system. Representative nitrogen heterocycles include pyridine, pyrrole, imidazole, triazole, tetrazole, morpholine, pyrrolidine, piperidine and piperazine. Suitable oxygen heterocycles include furan, tetrahydrofuran and dioxane. Sulfur heterocycles may include thiophene and tetrahydrothiophene.

Counterion X may be selected from chloride, bromide, sulfate, methosulfate, sulfonate, p-toluenesulfonate, borontetrafluoride,  $PF_6^-$ , phosphate and cyano radicals.

- 5 The term "substituted" is defined in relation to  $R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$  as a substituent which is a nitro, halo, cyano,  $C_1-C_{20}$  alkyl, amino, aminoalkyl, thioalkyl, sulfoalkyl, carboxyester, hydroxy,  $C_1-C_{20}$  alkoxy, polyalkoxy or  $C_1-C_{40}$  quaternary di- or tri-alkylammonium function.

10 The most preferred quaternary imine salts are the 3,4-dihydroisoquinolinium salts of structure II where  $R^5$  and  $R^6$  are defined by the same radicals as those for  $R^2$ :

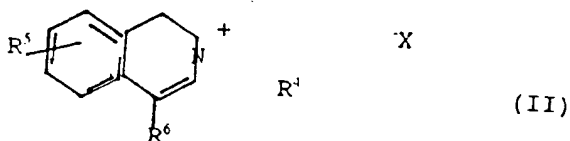


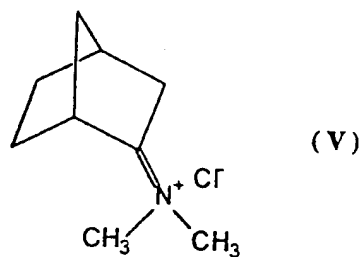
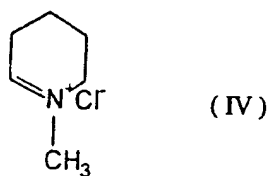
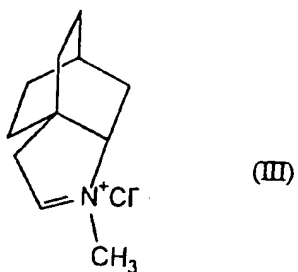
Table I lists specific illustrative compounds represented by structure II.

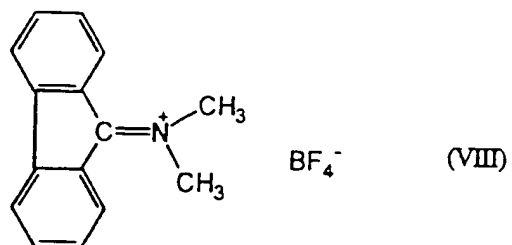
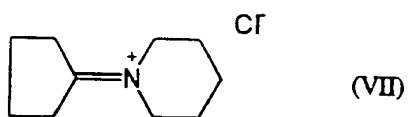
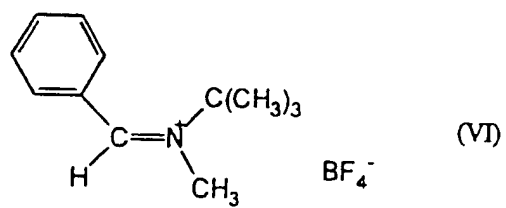


TABLE I

Compound	R <sup>4</sup>	R <sup>5</sup>	R <sup>6</sup>	X <sup>-</sup>
1	CH <sub>3</sub>	H	H	BF <sub>4</sub> <sup>-</sup>
2	CH <sub>3</sub>	H	H	p-tosylate
3	CH <sub>3</sub>	CH <sub>3</sub>	H	Cl <sup>-</sup>
4	CH <sub>3</sub>	NO <sub>2</sub>	H	Br <sup>-</sup>
5	CH <sub>3</sub>	Cl	H	BF <sub>4</sub> <sup>-</sup>
6	CH <sub>3</sub>	OCH <sub>3</sub>	H	brosylate <sup>-</sup>
7	phenyl	H	H	CH <sub>3</sub> SO <sub>4</sub> <sup>-</sup>
8	benzyl	phenyl	H	Cl <sup>-</sup>
9	(CH <sub>2</sub> ) <sub>2</sub> OH	CN	H	PF <sub>6</sub> <sup>-</sup>
10	CH <sub>3</sub>	CH <sub>2</sub> COCH <sub>3</sub>	H	PF <sub>6</sub> <sup>-</sup>
11	(CH <sub>3</sub> ) <sub>2</sub> CH	COCH <sub>3</sub>	H	CH <sub>2</sub> CH <sub>3</sub> SO <sub>4</sub> <sup>-</sup>
12	CH <sub>3</sub>	SO <sub>2</sub> Na <sup>+</sup>	H	Cl <sup>-</sup>
13	(CH <sub>3</sub> (CH <sub>2</sub> ) <sub>11</sub>	H	H	p-tosylate <sup>-</sup>
14	(CH <sub>3</sub> (CH <sub>2</sub> ) <sub>15</sub>	Br	H	CH <sub>2</sub> SO <sub>4</sub> <sup>-</sup>
15	CH <sub>2</sub> CH <sub>2</sub> N(CH <sub>2</sub> ) <sub>3</sub>	H	H	Cl <sup>-</sup>
16	CH <sub>3</sub>	F	H	Cl <sup>-</sup>
17	CH <sub>3</sub>	CF <sub>3</sub>	H	PF <sub>6</sub> <sup>-</sup>
18	CH <sub>3</sub>	CH <sub>2</sub> OPO <sub>3</sub> Na <sub>2</sub>	H	Cl <sup>-</sup>
19	CH <sub>3</sub>	pyridyl	H	Cl <sup>-</sup>
20	2-pyridyl	H	H	Cl <sup>-</sup>
21	CH <sub>3</sub>	CH <sub>2</sub> N <sup>+</sup> (CH <sub>3</sub> ) <sub>3</sub>	H	CH <sub>3</sub> SO <sub>4</sub> <sup>-</sup>
22	CH <sub>3</sub> CH <sub>2</sub> O(CH <sub>2</sub> ) <sub>7</sub>	H	H	CH <sub>3</sub> SO <sub>4</sub> <sup>-</sup>
23	CH <sub>3</sub>	(CH <sub>2</sub> ) <sub>7</sub> CH <sub>3</sub>	H	Cl <sup>-</sup>
24	CH <sub>3</sub>	CO <sub>2</sub> Na <sup>+</sup>	H	Cl <sup>-</sup>
25	(CH <sub>2</sub> ) <sub>7</sub> CH <sub>3</sub>	H	H	p-tosylate <sup>-</sup>
26	CH <sub>3</sub>	H	CH <sub>3</sub>	Cl <sup>-</sup>
27	CH <sub>3</sub>	H	phenyl	Cl <sup>-</sup>

Additional compounds according to the present invention are outlined below as structures III through X.

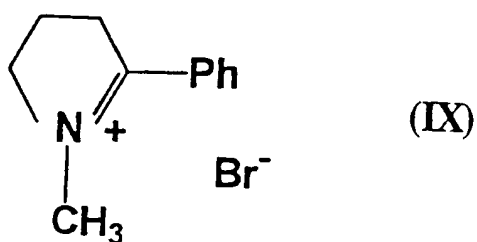




5

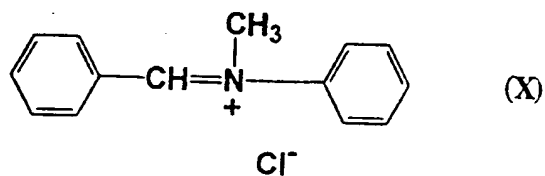
10

15



20

25



30

The foregoing oxygen transfer agents may be incorporated into detergent bleach compositions along with a further essential component which is a peroxygen compound capable of yielding peroxide anion in an aqueous solution.

Amounts of oxygen transfer agent suitable for the present invention may range from about 0.01 to 10%, preferably from about 0.2 to 5%, optimally from about 0.5 to 1.5% by weight of the composition.

5

The peroxygen compound may be present from about 1 to 60%, preferably from about 1.5 to 25%, optimally from about 2 to 10% by weight.

- 10 The molar ratio of peroxide anion (or a peroxygen compound generating the equivalent amount of peroxide anion) to oxygen transfer agent will range from about 1500:1 to about 1:2, preferably from about 150:1 to 1:1, optimally from about 60:1 to 3:1.

15

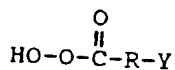
Peroxide anion sources are well known in the art. They include the alkali metal peroxides, organic peroxides such as urea peroxide, and inorganic persalts, such as the alkali metal perborates, percarbonates, perphosphates, persilicates and persulfates. Mixtures of two or more such compounds may also be suitable. Particularly preferred are sodium perborate tetrahydrate and, especially, sodium perborate monohydrate. Sodium perborate monohydrate is preferred because it has excellent storage stability while also dissolving very quickly in aqueous solutions.

Alkyl hydroperoxides are another suitable class of peroxygen compounds. Examples of these materials include cumene hydroperoxide and t-butyl hydroperoxide.

30

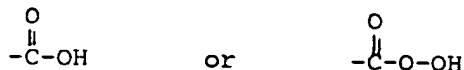
Organic peroxyacids may also be suitable as the peroxygen compound. Such materials have a general formula:

35



wherein R is an alkylene or substituted alkylene group containing from 1 to about 22 carbon atoms or a phenylene or substituted phenylene group, and Y is hydrogen, halogen, alkyl, aryl or

5

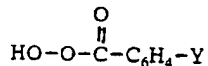


The organic peroxyacids usable in the present invention can contain either one or two peroxy groups and can be either aliphatic or aromatic. When the organic peroxyacid is aliphatic, the unsubstituted acid has the general formula:



where Y can be, for example, H, CH<sub>3</sub>, CH<sub>2</sub>Cl, COOH, or COOOH; and n is an integer from 1 to 20.

When the organic peroxy acid is aromatic, the unsubstituted acid has the general formula:



wherein Y is hydrogen, alkyl, haloalkyl, halogen or COOH or COOOH.

Typical monoperoxyacids useful herein include alkyl peroxyacids and aryl peroxyacids such as:

- (i) peroxybenzoic acid and ring-substituted peroxybenzoic acid, e.g. peroxy- $\alpha$ -naphthoic acid;
- (ii) aliphatic, substituted aliphatic and arylalkyl monoperoxy acids, e.g. peroxy lauric acid, peroxy stearic acid, and N,N-phthaloylaminoperoxy caproic acid (PAP); and
- (iii) amidoperoxyacids, e.g. monononylamide of either peroxysuccinic acid (NAPSA) or of peroxyadipic acid (NAPAA).

Typical diperoxyacids useful herein include alkyl diperoxyacids and aryldiperoxy acids, such as:

- (i) 1,12-diperoxydodecanedioic acid;
- (ii) 1,9-diperoxyazelaic acid;
- 5 (iii) diperoxybrassylic acid; diperoxysebacic acid and diperoxyisophthalic acid;
- (iv) 2-decyldiperoxybutane-1,4-dioic acid;
- (v) 4,4'-sulfonylbisperoxybenzoic acid; and
- (vi) N,N'-terephthaloyl-di(6-aminoperoxy-caproic acid)
- 10 (TPCAP).

Particularly preferred organic acids are peracetic acid, monoperoxyphthalic acid (magnesium salt hexahydrate), PAP, TPCAP and diperoxydodecanedioic acid. Under certain  
15 circumstances, hydrogen peroxide itself may directly be employed as the peroxygen compound.

Bleach systems of the present invention may be employed for a wide variety of purposes, but are especially useful in  
20 the cleaning of laundry. When intended for such purpose, the peroxygen compound and oxygen transfer agent of the present invention will usually also be combined with surface-active materials, detergency builders and other known ingredients of laundry detergent formulations.

25 The surface-active material may be naturally derived, such as soap or a synthetic material selected from anionic, nonionic, amphoteric, zwitterionic, cationic actives and mixtures thereof. Many suitable actives are commercially available and are fully described in the literature, for  
30 example in "Surface Active Agents and Detergents", Volumes I and II, by Schwartz, Perry and Berch. The total level of the surface-active material may range up to 50% by weight, preferably being from about 1% to about 40% by weight of  
35 the composition, most preferably 4 to 25%.

Synthetic anionic surface-actives are usually water-soluble alkali metal salts of organic sulfates and sulfonates having alkyl radicals containing from about 8 to about 22 carbon atoms.

5

Examples of suitable synthetic anionic detergent compounds are sodium and ammonium alkyl sulfates, especially those obtained by sulfating higher ( $C_8-C_{18}$ ) alcohols produced, for example, from tallow or coconut oil; sodium and ammonium alkyl ( $C_9-C_{20}$ ) benzene sulfonates, particularly sodium linear secondary alkyl ( $C_{10}-C_{15}$ ) benzene sulfonates; sodium alkyl glyceryl ether sulfates, especially those ethers of the higher alcohols derived from tallow or coconut oil and synthetic alcohols derived from petroleum; sodium coconut oil fatty acid monoglyceride sulfates and sulfonates; sodium and ammonium salts of sulfuric acid esters of higher ( $C_9-C_{18}$ ) fatty alcohol-alkylene oxide, particularly ethylene oxide reaction products; the reaction products of fatty acids such as coconut fatty acids esterified with isethionic acid and neutralized with sodium hydroxide; sodium and ammonium salts of fatty acid amides of methyl taurine; alkane monosulfonates such as those derived by reacting alpha-olefins ( $C_8-C_{20}$ ) with sodium bisulfite and those derived by reacting paraffins with  $SO_2$  and  $Cl_2$  and then hydrolyzing with a base to produce a random sulfonate; sodium and ammonium  $C_7-C_{12}$  dialkyl sulfosuccinates; and olefinic sulfonates, which term is used to describe the material made by reacting olefins, particularly  $C_{10}-C_{20}$  alpha-olefins, with  $SO_3$  and then neutralizing and hydrolyzing the reaction product. The preferred anionic detergent compounds are sodium ( $C_{11}-C_{15}$ ) alkylbenzene sulfonates; sodium ( $C_{16}-C_{18}$ ) alkyl sulfates and sodium ( $C_{16}-C_{18}$ ) alkyl ether sulfates.

35 Examples of suitable nonionic surface-active compounds which may be used preferably together with the anionic surface-active compounds include, in particular, the



reaction products of alkylene oxides, usually ethylene oxide, with alkyl ( $C_6-C_{22}$ ) phenols, generally 2-25 EO, i.e. 2-25 units of ethylene oxide per molecule; the condensation products of aliphatic ( $C_8-C_{18}$ ) primary or secondary linear or branched alcohols with ethylene oxide, generally 2-30 EO, and products made by condensation of ethylene oxide with the reaction products of propylene oxide and ethylenediamine. Other so-called nonionic surface-actives include alkyl polyglycosides, polyhydroxy fatty acid amides (e.g.  $C_{12}-C_{18}$  N-methyl glucamide), long-chain tertiary amine oxides, long-chain tertiary phosphine oxides and dialkyl sulfoxides.

Amounts of amphoteric or zwitterionic surface-active compounds can also be used in the compositions of the invention but this is not normally desired owing to their relatively high cost. If any amphoteric or zwitterionic detergent compounds are used, it is generally in small amounts in compositions based on the much more commonly used synthetic anionic and nonionic actives.

Soaps may also be incorporated into the compositions of the invention, preferably at a level of less than 30% by weight. They are particularly useful at low levels in binary (soap/anionic) or ternary mixtures together with nonionic or mixed synthetic anionic and nonionic compounds. Soaps which are used are preferably the sodium or, less desirably potassium, salts of saturated or unsaturated  $C_{10}-C_{24}$  fatty acids or mixtures thereof. The amount of such soaps can be varied between about 0.5 and about 25% by weight, with lower amounts of about 0.5 to about 5% being generally sufficient for lather control. Amounts of soap between about 2 and about 20%, especially between about 5 and about 15%, are used to give a beneficial effect on detergency. This is particularly valuable in compositions used in hard water when the soap acts as a supplementary builder.

The detergent compositions of the invention will normally also contain a detergency builder. Builder materials may be selected from (1) calcium sequestrant materials; (2) precipitating materials; (3) calcium ion-exchange materials; and (4) mixtures thereof.

In particular, the compositions of the invention may contain any one of the organic or inorganic builder materials, such as sodium or potassium tripolyphosphate, sodium or potassium pyrophosphate, sodium or potassium orthophosphate, sodium carbonate, the sodium salt of nitrilotriacetic acid, sodium citrate, carboxymethylmalonate, carboxymethyloxysuccinate, tartrate mono- and di-succinates, oxydisuccinate, crystalline or amorphous aluminosilicates and mixtures thereof.

Polycarboxylic homo- and copolymers may also be included as builders and to function as powder structurants or processing aids. Particularly preferred are polyacrylic acid (available under the trademark Acrysol from the Rohm and Haas Company) and acrylic-maleic acid copolymers (available under the trademark Sokalan from the BASF Corporation) and alkali metal or other salts thereof.

These builder materials may be present at a level of, for example, from 1 to 80% by weight, preferably from 10 to 60% by weight.

Upon dispersal in a wash water, the initial amount of peroxygen compound should range in amount to yield anywhere from about 0.05 to about 250 ppm active oxygen per liter of water, preferably between about 1 to 50 ppm. Within the wash media, the amount of oxygen transfer agent initially present should be from about 0.01 to about 300 ppm, preferably from about 1 to 100 ppm. Surfactant should be present in the wash water from about 0.05 to 1.0 grams per liter, preferably from 0.15 to 0.20 grams per liter. When

present, the builder amount will range from about 0.1 to 3.0 grams per liter.

Apart from the components already mentioned, the detergent compositions of the invention can contain any of the conventional additives in the amounts in which such materials are normally employed in detergent compositions. Examples of these additives include lather boosters such as alkanolamides, particularly the monoethanolamides derived from palmkernel fatty acids and coconut fatty acids, lather depressants such as alkyl phosphates and silicones, antiredeposition agents such as sodium carboxymethylcellulose and alkyl or substituted alkylcellulose ethers, other stabilizers such as ethylenediaminetetraacetic acid, fabric softening agents, inorganic salts such as sodium sulfate and, usually present in very small amounts, fluorescent whitening agents, perfumes, enzymes such as proteases, cellulases, lipases and amylases, germicides and colorants.

Stained consumer products benefiting from treatment with compositions of this invention may include clothes and other fabrics; household fixtures and appliances such as sinks, toilet bowls and oven ranges; tableware such as drinking glasses, dishes, cookware and utensils; and even dentures. Hair colorants may also be formulated with the bleach composition of this invention. The bleaching system of this invention may also be applied to industrial uses such as for the bleaching of wood pulp.

The system of the present invention may be delivered in a variety of product forms including powders, on sheets or other substrates, in pouches, in tablets, in aqueous liquids, or in non-aqueous liquids such as liquid nonionic detergents.

The following examples will more fully illustrate the embodiments of this invention. All parts, percentages and proportions referred to herein and in the appended claims are by weight unless otherwise illustrated.

EXAMPLE 13,4-Dihydroisoquinoline

The title compound was prepared, using the procedure of Yamazaki, Chem. Lett. (1992) 823. The starting reagent 1,2,3,4-tetrahydroisoquinoline was distilled under vacuum at 85°C (~10 mm Hg) prior to use.

Into a 3-necked 12 L Morton flask equipped with a mechanical stirrer were placed 1,2,3,4-tetrahydroisoquinoline (66.6 grams, 0.5 mol) and 2 liters of methylene chloride. A solution of potassium persulfate (189.23 grams, 0.7 mol), sodium hydroxide (48 grams, 1.2 mol) and water (4.4 L) was added. While the solution was vigorously mixed, a 0.05 M aqueous solution of nickel sulfate hexahydrate (200 ml, 0.01 mol) was added to the biphasic mixture. Fine black precipitates deposited immediately, and the resulting mixture was stirred vigorously at room temperature. The reaction temperature became slightly elevated to about 35°C. After 3.5 hours of stirring, the black color changed to a light brown colored solution. The mixture was filtered through a short Celite frit column to remove any insoluble materials. The organic layer in the filtrate was separated by extraction with methylene chloride. The organic layer was dried over magnesium sulfate and concentrated down to give 56 g (85% yield) of a dark red liquid. Distillation at 105°C under vacuum (~11 mm Hg) provided 46 g (70%) of a yellow liquid.

The sample contained two impurities: 4% of isoquinoline and 1% of unreacted 1,2,3,4-tetrahydroisoquinoline.

<sup>1</sup>H NMR (CDCl<sub>3</sub>/TMS): δ 2.73 (t, 2H) 3.77 (t, 2H), 7.09-7.37 (m, 4H), 8.33 (s, 1H). The isoquinoline is shown at δ 3.10 (t, 2H), 4.01 (s, 2H) 7.59-7.94 (m, 4H), 8.51 (d, 2H) and 9.25 (s, 1H).

N-Methyl-3,4-dihydroisoquinolinium p-toluenesulfonate  
(Imine Quat OTs)

The title compound was prepared, using the procedure described by Koelsch et al. in J. Am. Chem. Soc. (1953) 75, 2095. In a 250-ml one-necked round-bottomed flask equipped with a magnetic stir bar and a reflux condenser were placed 3,4-dihydroisoquinoline (8.27 grams, 63 mmol) and 40 ml of methanol. The mixture was stirred and cooled to 0°C. A solution of methyl p-toluenesulfonate (11.73 g, 63 mmol) and 70 ml of methanol was added dropwise. The color of the solution remained clear and yellow. The mixture was heated to reflux for 6 hours. The methanol was then removed *in vacuo* to provide a quantitative yield (20 g) of an off-white solid (mp 115-119°C). The solid was pulverized and washed with 40 ml of acetone at room temperature.

Suction filtration provided a white solid in 88% yield: mp 124-127°C.

<sup>1</sup>H NMR (D<sub>2</sub>O): δ 2.27 (s, 3H), 3.15 (t, 2H), 3.73 (s, 3H), 3.93 (t, 2H), 7.18-7.78 (m, 8H), 8.77 (s, 1H). Impurities observed at 4.46 (s), 8.0-8.3 (m), 9.4 (s) were due to N-methyl-isoquinolinium p-toluenesulfonate.

EXAMPLE 2

N-Methyl-3,4-dihydroisoquinolinium borontetrafluoride  
(Imine Quat BF<sub>4</sub>)

The title compound was prepared according to the literature procedure (Hanquet, G., Lusinchi X., Milliet, P., Tetrahedron Letters, (1988), 29, 3941).

In a 50 mL 2-necked round-bottomed flask equipped with a reflux condenser and stir bar under nitrogen were placed 3,4-dihydroisoquinoline (1.0 g, 7.6 mmol) and 30 mL of anhydrous toluene. Once in solution, trimethyloxonium tetrafluoroborate (1.12 g, 7.6 mmol) was added, which was not soluble in toluene. The reaction mixture was stirred at

room temperature for 10 hours. The reaction mixture was separated into two levels. The dark-red brown viscous liquid was decanted out and dried in an oven to remove any excess toluene.

5

$^1\text{H}$  NMR (DMSO/TMS):  $\delta$  3.23 (2H,m), 3.73 (3H,s), 4.02 (2H,s), 7.47-7.82 (4H,m) and 9.18(1H,s).

### EXAMPLE 3

10

#### N-(n-Octyl)-3,4-Dihydroisoquinoline p-toluenesulfonate (Octyl Quat OTs)

3,4-Dihydroisoquinoline (1.31 g, 10.0 mmol) was dissolved in 3 ml MeOH in a 3-neck 25 ml round bottom flask fitted with a condenser, drying tube and stirrer bar, and cooled in an ice bath. n-Octyl p-toluenesulfonate (2.84 g, 10.0 mmol)\*, dissolved in 7.0 ml methanol, was added dropwise over about 7 minutes via an addition funnel. The ice bath was removed and replaced with an oil bath and the colorless clear solution heated to reflux for at least 8 hours during which time the reaction solution turned yellow. Removal of the methanol *in vacuo* gave slightly colored solid product which was triturated with about 7.5 ml acetone. The acetone insoluble solids were filtered, washed with more acetone and dried in a vacuum desiccator. Yield of colorless solids was 1.91 g. A second batch of solids was recovered from the acetone filtrate/washing and filtered, washed with acetone and dried to give 0.31 gm colorless solids.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 200 MHz)  $\delta$  9.70 (1H, s, C<sub>1</sub>), 7.00-8.10 (8H, m), 4.20 (2H, t), 4.00 (2H, t), 3.25 (2H, t), 2.30 (3H, s), 1.80 (2H, m), 1.20 (10H, m), 0.87 (3H, t).

\*C.S.Marvel and V.C.Seker, Org. Syn., Coll. Vol. III (1955), p. 366.

35

EXAMPLE 4

Stain bleaching experiments were conducted in a Terg-O-Tometer in 500 mL of milli-Q water, using two tea-stained  
5 cotton cloths measuring 3x4 inches. In a typical test, 0.75 g of commercial detergent was added to the system and the pH of the solution was constantly buffered to the indicated level by the addition of dilute aqueous sodium hydroxide or hydrochloric acid. A given oxidant was then added to the  
10 system, followed by an appropriate amount of quaternary imine salt. Washes were carried out at the indicated temperature for 15 minutes.

Stain bleaching was measured reflectometrically, using a  
15 Colorgard System/05 Reflectometer.  $\Delta R$  is the reflectance difference between washed and unwashed cloths; effects due to detergent are not subtracted. Bleaching was indicated by an increase in reflectance, reported as  $\Delta\Delta R$ . In general, a  $\Delta\Delta R$  of one unit is perceivable in a paired comparison while  
20  $\Delta\Delta R$  of two units is perceivable monadically.

Table II and III report the bleaching activity of the N-methyl-3,4-dihydroisoquinoline borontetrafluoride ( $BF_4$ ) and p-toluenesulfonate (OTs) salts.



TABLE II  
Tea Stain (BC-1) at pH 10 and 18°C

BASE*	PEROXIDE (10 ppm a.o)	SALT COUNTERION	IMINE QUAT SALT CONCENTRATION	ΔR PEROXIDE	ΔR IMINE QUAT SALT & PEROXIDE	ΔΔR IMINE QUAT SALT
P-SURF®	OXONE	BF <sub>4</sub>	6.0X10 <sup>-6</sup> M	0.58	10.54	9.96
P-SURF®	OXONE	BF <sub>4</sub>	6.0X10 <sup>-6</sup> M	1.16	7.24	6.08
ULTRA SURF®	OXONE	BF <sub>4</sub>	6.0X10 <sup>-6</sup> M	0.60	5.19	4.59
ULTRA ALL®	OXONE	BF <sub>4</sub>	6.0X10 <sup>-6</sup> M	0.84	5.99	5.15

\*P-Surf® : Anionic/nonionic/phosphate builder; dosage 1.5 g/l.

10 Ultra-Surf® : 15% anionic/8% nonionic/30% zeolite/20% carbonate; dosage 1.02-1.1 g/l.

Ultra-All® : 14% anionic/38% carbonate/29% sulfate; dosage 1.02-1.1 g/l.

TABLE III

Tea Stain (BC-1) at varying pH and 10°C

BASE	PEROXIDE	pH	SALT COUNTERION	IMINE QUAT SALT CONCENTRATION	$\Delta R$ IMINE PEROXIDE	$\Delta \Delta R$ IMINE QUAT SALT & PEROXIDE	$\Delta \Delta \Delta R$ IMINE QUAT SALT
ULTRA SURF®	OXONE	10.0	OTs	$6.0 \times 10^{-5} M$	-	11.2	-
ULTRA SURF®	PAP*	9.5	OTs	$6.0 \times 10^{-5} M$	5.3	13.2	7.9

\*N,N-phthaloylamino-peroxycaproic acid.

Based on the results in Tables II and III, it is evident that the imine quat salts have a pronounced effect upon improving bleaching of a tea-stained cloth. Different formulated base powders have a relatively small effect on the bleaching performance of the imine quat salt.

#### EXAMPLE 5

This Example illustrates the effect of pH upon a system utilizing the imine quat salt of Example 1 and PAP as the peroxide source. There is relatively little change with respect to bleaching performance over the pH range 8.0 to 10.0.

TABLE IV

Tea-stained Cloth at an 18°C Wash Temperature

pH	IMINE QUAT SALT CONCENTRATION	$\Delta R$ PEROXIDE	$\Delta R$ IMINE QUAT SALT & PEROXIDE	$\Delta \Delta R$ IMINE QUAT SALT
8.0	$6.0 \times 10^5 M$	5.60	14.0	8.40
9.0	$6.0 \times 10^5 M$	4.90	13.0	8.10
10.0	$6.0 \times 10^5 M$	4.20	12.3	8.10

#### EXAMPLE 6

This Example details the effect against stains other than that of tea. Table V establishes that the imine quat salt of Example 2 enhances the bleaching performance of OXONE against a spaghetti sauce stain.

TABLE V

Spaghetti Sauce-stained Cloth at an 18°C Wash Temperature

5	BASE	PEROXIDE	IMINE QUAT SALT CONCENTRATION	$\Delta R$ PEROXIDE	$\Delta R$ IMINE QUAT SALT & PEROXIDE	$\Delta\Delta R$ IMINE QUAT SALT
	ULTRA ALL®	OXONE	$6.0 \times 10^{-4} M$	13.65	16.53	2.88

10 Wine (EMPA-114) stains were found to be effectively removed by the imine quat salt of Example 1 in combination with PAP as the peroxide source. Table VI outlines these results.

TABLE VI

15 Wine-stained Cloth at an 18°C Wash Temperature

20	BASE	PEROXIDE	IMINE QUAT SALT CONCENTRATION	$\Delta R$ PEROXIDE	$\Delta R$ IMINE QUAT SALT & PEROXIDE	$\Delta\Delta R$ IMINE QUAT SALT
	ULTRA ALL®	PAP	$6.0 \times 10^{-4} M$	14.8	18.1	3.3

EXAMPLE 7

25 This Example illustrates the performance of the octyl imine quat salt of Example 3 and PAP as the peroxide source. Surprisingly, at lower temperatures, the performance was better than at higher wash temperatures.

TABLE VII

Tea Stain (BC-1) Bleaching Performance of Octyl Quat  
pH 9.5, 1.02 g/l Ultra All®, 15-minute wash

TEMP. (0°C)	PAP (7.5 ppm a.o)	$\Delta R$ PAP	$\Delta R$ PAP + OCTYL IMINE QUAT CONCENTRATION		
			$6 \times 10^{-6} M$	$2 \times 10^{-5} M$	$6 \times 10^{-5} M$
10	Powder in DMF	2.1	6.2	8.3	9.6
10	Granule	3.7	7.8	10.3	12.1
32	Powder in DMF	4.1	5.6	6.1	6.9
32	Granule	5.6	6.4	7.4	9.5

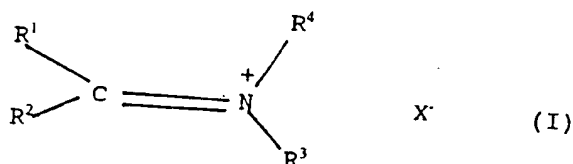
The foregoing description and Examples illustrate selected  
embodiments of the present invention. In light thereof,  
various modifications will be suggested to one skilled in  
the art, all of which are within the spirit and purview of  
this invention.

CLAIMS

1. A bleaching composition comprising:

(i) from about 1 to about 60% by weight of a peroxygen  
5 compound;

(ii) from about 0.01 to about 10% of an oxygen transfer  
agent whose structure is:



wherein:

R<sup>1</sup> and R<sup>4</sup> may be a substituted or unsubstituted radical  
selected from the group consisting of hydrogen, phenyl,  
aryl, heterocyclic ring, alkyl and cycloalkyl radicals;

20 R<sup>2</sup> may be a substituted or unsubstituted radical selected  
from the group consisting of hydrogen, phenyl, aryl,  
heterocyclic ring, alkyl, cycloalkyl, nitro, halo, cyano,  
alkoxy, keto, carboxylic and carboalkoxy radicals;

R<sup>3</sup> may be a substituted or unsubstituted radical selected  
25 from the group consisting of phenyl, aryl, heterocyclic  
ring, alkyl, cycloalkyl, nitro, halo, and cyano radicals;

R<sup>1</sup> with R<sup>2</sup> and R<sup>2</sup> with R<sup>3</sup> may respectively together form a  
radical selected from the group consisting of cycloalkyl,  
polycyclo, heterocyclic and aromatic ring systems;

30 X is a counterion stable in the presence of oxidizing  
agents; and

(iii) from about 0.5 to 50% of a surfactant.

2. A composition according to claim 1, further  
35 comprising from about 1 to about 80% of a detergent  
builder.

3. A composition according to claim 1, further comprising an effective amount for cleaning of an enzyme selected from the group consisting of proteases, cellulases, lipases, amylases and mixtures thereof.
- 5 4. A composition according to claim 1 delivered in a form selected from the group consisting of a powder, sheet, pouch, tablet, aqueous liquid and non-aqueous liquid.
- 10 5. A composition according to claim 1 wherein the peroxygen compound is present in an amount from about 1.5 to 25% and the oxygen transfer agent is present in an amount from about 0.2 to 5% by weight.
- 15 6. A composition according to claim 1 wherein the peroxygen compound is an inorganic material selected from the group consisting of perborate, percarbonate, perphosphate, persilicate and monopersulphate salts.
- 20 7. A composition according to claim 1 wherein the peroxygen compound is an organic peroxyacid.
8. A composition according to claim 5 wherein the organic peroxyacid is selected from the group consisting of  
25 peracetic acid, monoperoxyphthalic acid, diperoxy dodecanedioic acid, N,N'-terephthaloyl-di(6-aminoperoxy caproic acid) and N,N'-phthaloylaminoperoxy caproic acid.
9. A composition according to claim 7 wherein the  
30 organic peroxyacid is an amidoperoxyacid.
10. A composition according to claim 1 wherein said substituent on R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup> and R<sup>4</sup> is a functional unit selected from the group consisting of nitro, halo, cyano,  
35 C<sub>1</sub>-C<sub>20</sub> alkyl, amino, aminoalkyl, thioalkyl, sulfoxyalkyl, carboxyester, hydroxy, C<sub>1</sub>-C<sub>20</sub> alkoxy, polyalkoxy, C<sub>1</sub>-C<sub>40</sub> quaternary di- or tri-alkylammonium functional units and

mixtures thereof.

11. A composition according to claim 1 wherein the oxygen transfer agent is 3,4-dihydroisoquinolinium salt.

5

12. A composition according to claim 11 wherein the salt is an N-methyl-3,4-dihydroisoquinolinium salt.

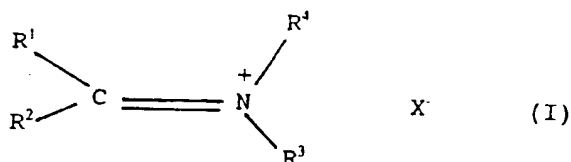
13. A composition according to claim 11 wherein the salt is an N-octyl-3,4-dihydroisoquinolinium salt.

10

14. A method for bleaching a stained substrate, said method comprising contacting said stained substrate in an aqueous medium with a peroxygen compound, a surfactant in an effective amount to clean said substrate and with an oxygen transfer agent whose structure is:

15

20



wherein:

25 R<sup>1</sup> and R<sup>4</sup> may be a substituted or unsubstituted radical selected from the group consisting of hydrogen, phenyl, aryl, heterocyclic ring, alkyl and cycloalkyl radicals;

R<sup>2</sup> may be a substituted or unsubstituted radical selected from the group consisting of hydrogen, phenyl, 30 aryl, heterocyclic ring, alkyl, cycloalkyl, nitro, halo, cyano, alkoxy, keto, carboxylic and carboalkoxy radicals;

R<sup>3</sup> may be a substituted or unsubstituted radical selected from the group consisting of phenyl, aryl, heterocyclic ring, alkyl, cycloalkyl, nitro, halo, and cyano radicals;

35 R<sup>1</sup> with R<sup>2</sup> and R<sup>2</sup> with R<sup>3</sup> may respectively together form a radical selected from the group consisting of cycloalkyl, polycyclo, heterocyclic and aromatic ring systems;

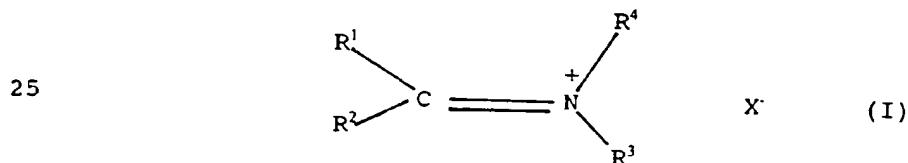
X<sup>-</sup> is a counterion stable in the presence of oxidizing agents; and said peroxygen compound to oxygen transfer agent



being present in a molar ratio ranging from about 1500:1 to about 1:2.

15. A method according to claim 14 wherein the ratio of  
5 peroxygen compound to oxygen transfer agent ranges from about 150:1 to 1:1.
16. A method according to claim 14 wherein said  
substrate is selected from the group consisting of fabrics,  
10 household fixtures and tableware.
17. A method according to claim 14 wherein said  
substrate is a denture.
- 15 18. A composition according to claim 14 wherein the  
oxygen transfer agent is a 3,4-dihydroisoquinolinium salt.

19. A method for bleaching a stained substrate, said  
method comprising contacting said stained substrate in an  
20 aqueous medium with a peroxygen compound and with an oxygen  
transfer agent whose structure is:



wherein:

- 30 R<sup>1</sup> may be a substituted or unsubstituted radical selected  
from the group consisting of hydrogen, phenyl, aryl,  
heterocyclic ring, alkyl and cycloalkyl radicals;
- R<sup>2</sup> may be a substituted or unsubstituted radical  
selected from the group consisting of hydrogen, phenyl,  
35 aryl, heterocyclic ring, alkyl, cycloalkyl, nitro, halo,  
cyano, alkoxy, keto, carboxylic and carboalkoxy radicals;
- R<sup>3</sup> may be a substituted or unsubstituted radical selected  
from the group consisting of phenyl, aryl, heterocyclic  
ring, alkyl, cycloalkyl, nitro, halo, and cyano radicals;

$R^1$  with  $R^2$  and  $R^2$  with  $R^3$  may respectively together form a radical selected from the group consisting of cycloalkyl, polycyclo, heterocyclic and aromatic ring systems;

$X^-$  is a counterion stable in the presence of oxidizing agents; and said contacting to achieve bleaching being performed in said medium containing about 0.05 to about 250 ppm active oxygen from the peroxygen compound and about 0.01 to about 300 ppm oxygen transfer agent.

20. A method according to claim 19 wherein the oxygen transfer agent is present from about 5 to about 100 ppm per liter of medium.

21. A method according to claim 19, further comprising from about 0.05 to about 1.0 grams surfactant per liter of medium.

# INTERNATIONAL SEARCH REPORT

Int. Appl. No.  
PCT/EP 94/03

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 6 C11D3/39

According to International Patent Classification (IPC) or to both national classification and IPC.

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 6 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US,A,5 041 232 (D.J. BATAL ET AL.) 20 August 1991 cited in the application see the whole document ---	1-7, 11, 14-21
A	US,A,4 210 551 (G.R. BRUBAKER ET AL) 1 July 1980 see claims ---	1, 2, 4-6, 14, 16, 19
A	US,A,4 194 987 (G.R. BRUBAKER ET AL) 25 March 1980 see claims ---	1, 2, 4-6, 14
A	FR,A,2 222 428 (AMERICAN CYANAMID) 18 October 1974 see claims; examples ---	1, 14
-/--		

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

### \* Special categories of cited documents :

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
- \*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

\*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

- \*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- \*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

\*&\* document member of the same patent family

Date of the actual completion of the international search

13 March 1995

Date of mailing of the international search report

17. 03. 95

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax (+31-70) 340-3016

Authorized officer

Grittern, A

# INTERNATIONAL SEARCH REPORT

Int. Application No.

PCT/EP 3656

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
------------	--	-----------------------

A	<p>DATABASE WPI  Derwent Publications Ltd., London, GB;  AN 90-249815  &amp; JP,A,2 173 098 (LION CORP) 4 July 1990  see abstract</p> <p>-----</p>	1,14
---	--	------

# INTERNATIONAL SEARCH REPORT

information on patent family members

International Application No.

PCT/EP 94/036

Patent document: cited in search report	Publication date	Patent family member(s)	Publication date
US-A-5041232	20-08-91	AU-B- 636724	06-05-93
		AU-A- 7287091	19-09-91
		CA-A- 2037800	17-09-91
		DE-D- 69104405	10-11-94
		DE-T- 69104405	09-02-95
		EP-A- 0453003	23-10-91
		ES-T- 2061156	01-12-94
		JP-A- 4227697	17-08-92
US-A-4210551	01-07-80	NONE	
US-A-4194987	25-03-80	NONE	
FR-A-2222428	18-10-74	US-A- 3824188	16-07-74
		AU-A- 6571974	21-08-75
		BE-A- 812561	20-09-74
		CA-A- 1022304	13-12-77
		DE-A- 2412954	26-09-74
		GB-A- 1424502	11-02-76
		JP-A- 49126580	04-12-74
		NL-A- 7403434	24-09-74

**THIS PAGE BLANK (USPTO)**